

California Environmental Protection Agency



Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

MLD SOP SAS 02

**STANDARD OPERATION PROCEDURE FOR THE
MEASUREMENT OF AMMONIUM ION IN AQUEOUS
CONSUMER PRODUCTS USING ION CHROMATOGRAPHY**

July 7, 2003, Revision 2.1

DISCLAIMER: Mention of any trade name or commercial product in Method 310 and associated Standard Operating Procedures does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

1 INTRODUCTION

This document describes a method for the determination of ammonia in consumer products. Ammonia has the potential to be counted as a VOC in the total volatile organic compounds analysis as determined by MLD SOP SAS 01. Ammonium hydroxide, with a vapor pressure of 115 mmHg at 20°C, is present in most glass cleaners and some general purpose cleaners and can potentially cause an overestimation in the VOC determination if not accounted for. The following procedure is designed to quantify ammonia at concentrations equal to or greater than 0.1 % by weight in consumer products. For more information see ASTM D 1426-93 or U.S. EPA Method 300.7.

2 SUMMARY OF METHOD

Ion chromatography with a conductivity detector is used to analyze the ammonium ion (NH_4^+) in consumer products. An aliquot of the product is diluted in water and introduced into the ion chromatograph via autosampler. The system is comprised of a guard column, an analytical column, a self-regenerating suppressor, and a conductivity detector.

3 INTERFERENCES AND LIMITATIONS

- 3.1 Interferences can be caused by retention times that are similar to and overlap that of the cation of interest. Large amounts of any given cation could interfere with the peak resolution of an ion. Sample dilution may address interference problems of this nature.
- 3.2 Interferences may be caused by contaminants in the reagent water, the reagents, glassware, and other sample processing apparatus that could lead to detectable concentrations of ions or an elevated baseline. A water blank is run at the beginning of each sample batch analysis to ascertain any possible contamination from reagents or sample vials used.

4 INSTRUMENTATION AND EQUIPMENT

- 4.1 The ion chromatographic system is comprised of modular units from Dionex Corporation. It is comprised of:

- LC20 Chromatography Enclosure
- GP50 Gradient Pump
- CD20 Conductivity Detector
- AS40 Automated Sampler

4.2 Column, Eluant, and Conditions:

IonPac CS12A 4 x 250 mm with an IonPac CG12 guard column, the eluant is 100% 20 mM methanesulfonic acid, with a flow rate of 1.0 ml/min. The suppressor is CSRS Ultra 4 mm.

Sample loop is 100 μ L and the expected background conductivity is < 1.0 μ S.

5 REAGENTS AND MATERIALS

- 5.1 Reagent grade, ASTM Type 1 deionized water, 18.0 M Ω
- 5.2 Ammonium ion standard from Alltech 1000 μ g/mL NIST-SRM traceable (Alltech cat. no. 37001)
- 5.3 Standard Solutions: Dilute 100 μ l, 500 μ l, and 1000 μ l of the NIST ammonium standard to 100 ml with deionized water. The instrument is calibrated to 1.0, 5.0, and 10.0 μ g/ml.
- 5.4 Control Sample: Dilute 500 μ L of the NIST ammonium standard to 100 ml. This corresponds to a concentration of 5.0 μ g/ml.
- 5.5 Dionex 5 mL sample vials with filter caps.

6 PROCEDURE

- 6.1 Turn on the pump and let the instrument equilibrate for about 30 minutes.
- 6.2 Three calibration standards are made from the 1000 μ g/mL stock standard. Prepare in a 100mL volumetric flask the standard as follows:

1.0 μ g/mL \cap 0.1 mL/100 ml

5.0 μ g/mL \cap 0.5 mL/100 ml

10.0 μ g/mL \cap 1.0 mL/100 ml

Transfer to a 5 mL sampler vial and cap.

- 6.3 Prepare a calibration check sample at 5.0 μ g/ml using a different source of the ion. The value of the calibration check sample must fall within $\pm 3s$ of the expected value. The calibration check sample is run after the calibration, every ten samples, and at the end of the sample batch.

- 6.4 Sample Measurements: The consumer products to be analyzed are prepared as a 1:10 weight/volume dilution in 1-methoxy-2-propanol (MPA). A 1.0 mL aliquot of the dilution is transferred to a 100 mL volumetric flask and brought to volume with deionized water. The now 1:1000 dilution of the sample is analyzed in the same manner as the standards.

7 QUALITY CONTROL

- 7.1 The weight fraction of ammonium in the liquid product is calculated as follows:

$$\text{Wt. fraction NH}_4 = \frac{(\text{Measured Concentration, } \mu\text{g/ml})}{\text{Weight Sample (g)}} \times 10^{-3}$$

SOP REVISION HISTORY

DATE	VERSION	NOTES
August 20, 1996	1	The samples will be prepared from the 1:10 dilutions in MPA. The samples are weighed 1.0 mL aliquots to 10 mL in MPA and 1.0 mL of this dilution is prepared for the ammonia analysis.
March 10, 1998	2	Adjusted document font to Times New Roman 12. Inserted appendix A which was formerly a stand-alone document.
June 20, 2001	3	SOP updated to reflect change in instrumentation. Ion Chromatography will now be used for the ammonia analysis. Changed font to Arial 12.
July 7, 2003	2.1	Corrected typographical errors. Corrected version enumeration.